

Alkaline hydrolysis of Procion Blue MX-R

Investigation of the hydrolysis of the reactive dyes was carried out by heating at 80°C, for 120 minutes, 10 mL of Procion Blue MX-R solution in NaHO 0.1M. After cooling and neutralization with HCl 1M, samples were diluted to 25 mL with acetate buffer 0.1M, pH 5. In figure 6 we can see the voltammograms obtained for a standard solution of Procion Blue MX-R, prepared by the same procedure, but without submission to hydrolysis (voltammogram 1) and for the hydrolysed solution (voltammogram 2). The loss of chlorotriazine peak and the appearance of a new peak, not yet characterised, for the hydrolysed solution can be important to monitor hydrolysis product in presence of these dyes.

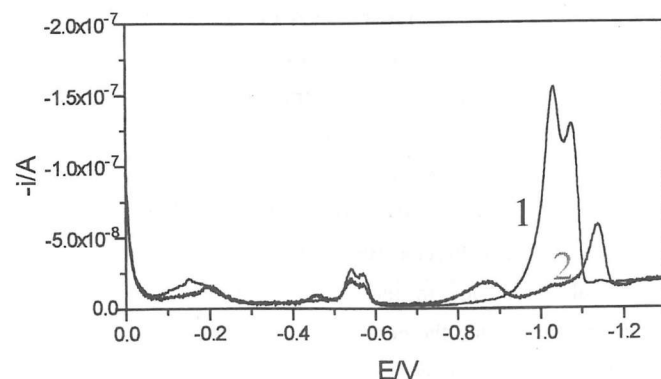


Fig. 6 - SW voltammograms obtained in the following situations: 1) for a standard solution of Procion Blue MX-R, 4×10^{-7} M; 2) for the hydrolysis solution (final conc. 4×10^{-7} M); Frequency, 100 Hz. Other conditions identical to fig. 1.

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ELECTROANALYTICAL DETERMINATION OF MOLINATE

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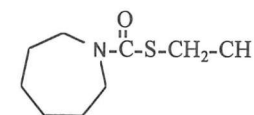
Abstract

The electrochemical oxidation of molinate, a thiocarbamate herbicide, has been studied in order to determine it in a phytopharmaceutical product. A square wave voltammetry electroanalytical method has been developed and the results were in good agreement with those obtained by the AOAC reference method using gas chromatography. The recovery is 100.2%.

Keywords: Molinate, thiocarbamate, herbicides, square wave voltammetry.

Introduction

Molinate is a thiocarbamate and its electrochemical oxidation has been studied with a view to its determination in a phytopharmaceutical mixture. It is one of the most successful herbicides that has been used in the treatment of rice crops. Due to possible contamination of water basins near the land where it is applied it is very important to develop fast and inexpensive methods for its quantification. It has the following molecular structure



Several analytical methods have been developed for the determination of molinate in different samples such as spectrophotometric methods [1], gas chromatography [1-5], liquid chromatography [5, 6], thin layer chromatography [1, 7-9] and immunoassays [10, 11].

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Experimental

Reagents and solutions

Molinate was from Riedel de Haen. The stock solution of molinate was prepared in acetonitrile at a concentration of 5.2×10^{-2} M. The buffer solutions used were in the pH range 1.9 to 12.0 [12]. Quantitative determinations were carried out in pH = 1.9 Britton-Robinson buffer. All reagents were analytical grade and aqueous solutions were prepared using purified water from a Millipore Milli-Q system (conductivity $< 0.1 \mu\text{S cm}^{-1}$).

Commercial sample preparation

Molinate was determined in a commercial product, Ordram. An amount of 0.91 g of Ordram was weighed and added to 25 mL of acetonitrile. This solution was placed in an ultrasound bath for 15 minutes and then more acetonitrile was added to make a final volume of 50.0 mL and the solution allowed to rest. From this sample stock solution aliquots were added to buffer electrolyte and used to prepare a sample with a concentration within the calibration curve range.

Apparatus

All experiments were performed using a 663 VA Metrohm system containing a glassy carbon working electrode (Metrohm 6.1204.000) ($d = 3.0$ mm), a glassy carbon rod counter electrode (Metrohm 6.1247.000) and a Ag/AgCl reference electrode (Metrohm 6.0728.000) attached to a Autolab PSTAT 10 potentiostat/galvanostat running with model GPES version 3 software, from Eco-Chemie, Netherlands. The square wave voltammetry conditions were frequency 50 Hz and amplitude 50 mV.

The glassy carbon working electrode was polished every day using a polishing kit (Metrohm 6.2802.010) first with $\alpha\text{-Al}_2\text{O}_3$ (0.3 μm) and water during 60 s and after with only water during 60 s. After polishing the electrode surface was thoroughly washed with purified water.

The pH measurements were obtained with a E 520 pH-meter from Metrohm with a combined glass electrode (Metrohm 6.0202.000).

For the experiments following the AOAC Reference Method [4] a Pye Unicam, Model GCD gas chromatograph was used with a Chrompack 3% silicon OV-17 column on a Gas Chrom Q 60-80 mesh 1.8 m x $\frac{1}{4}$ " x 4 mm SS.

Results and Discussion

The electrochemical behaviour of molinate was investigated over a large pH range between 1.9 and 12.0 at a glassy carbon working electrode, using differential pulse voltammetry and scanning from +1.0 to +1.8 V. The oxidation of molinate occurs at +1.6 V vs. Ag/AgCl and was studied using cyclic, differential pulse and square wave voltammetry; it is an irreversible process. For pH values between 1.9 and 4.0 there was no variation in the peak potential but the peak currents decreased rapidly. For higher pH values the wave definition was very poor and only a shoulder could be found. So the optimal pH for the supporting electrolyte Britton-Robinson buffer solution was found to be 1.9 and a square wave voltammetry electroanalytical method has been developed.

In order to enhance the peak current and reproducibility an electrochemical treatment was applied to the electrode surface. It consisted of the application of a constant potential of -1.5 V during 1 second followed by five potential scans between +1.0 and +1.8 V. This treatment was applied before each voltammogram.

The electroanalytical method developed for the determination of molinate was used to analyse a commercial compound, Ordram, that contains molinate as the active ingredient. The sample and calibration standards, between 4.96×10^{-4} and 9.02×10^{-4} M, were prepared according to the description in the experimental section. The square wave voltammograms obtained for sample and standards are in Fig. 1. The calibration plot showed a straight line ($r = 0.998$, $n = 5$) for molinate.

The results obtained with the electrochemical method were compared with those obtained by the AOAC method, they were in good agreement and the reproducibility was good. The AOAC method [4] is a gas chromatographic procedure for measuring molinate in commercial herbicide products and aqueous formulations.

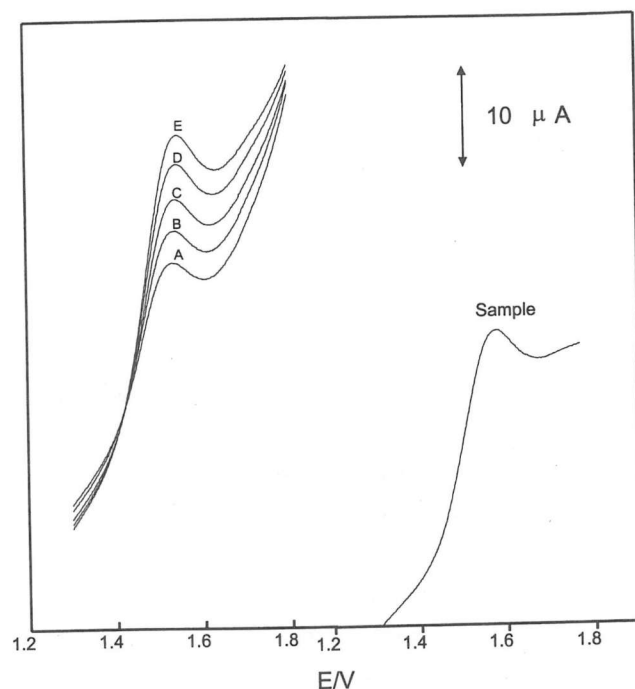


Fig.1 Square wave voltammograms of molinate at pH = 1.9, frequency 50 Hz and pulse amplitude 50 mV. Successive additions of standard solutions for constructing the calibration plot (A – 4.961×10^{-4} , B – 5.983×10^{-4} , C – 7.000×10^{-4} , D – 8.015×10^{-4} , E – 9.024×10^{-4} M) and commercial sample.

The mean and relative standard deviation obtained for 5 determinations by the electrochemical method were 7.4% w/w and 2.0% respectively and by the AOAC procedure 7.3% w/w and 1.6%. The recovery data for these 5 determinations using the electrochemical method was 100.2%. The accuracy of these results was assessed by comparing the electrochemical results with those obtained by the AOAC method, the relative error being 1.6%.

Conclusions

The electrochemically-developed method can be successfully used to quantify the herbicide molinate in a phytopharmaceutical product. It is simple, enables a faster determination than the conventional method and is not expensive. A comparative evaluation of the data showed that the results obtained electroanalytically were in good agreement with those obtained by the AOAC chromatographic method (relative error 1.6%) and mean recovery index of 100.2%.

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